

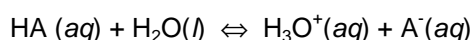
Determination of the Identity of an Unknown Weak Acid

Adapted from R. C. Kerber et. al http://www.sinc.sunysb.edu/Class/orgolab/che199_susb014.PDF; W.F. Kinard et.al <http://www.cofc.edu/~kinard/221LCHEM/2002CHEM221LabSchedule.htm>; and D.C. Harris Quantitative Chemical Analysis, 5th ed Freeman Press, 1998.

Introduction:

The purpose of this exercise is to identify an unknown weak acid by titration with a standard sodium hydroxide solution. The pH of the titration solution will be monitored using a pH meter; the obtained titration plot will then be used to determine the equivalent molecular weight and dissociation constant (K_a) of the unknown. These values will then let you decide the identity of the weak acid.

When a weak acid, HA, is dissolved in water, only some of the molecules dissociate to yield H_3O^+ and A^- ions. At this point, a dynamic equilibrium is established:



Under these equilibrium conditions, the total concentration of each species remains constant, even though the species in solution are constantly dissociating and recombining. The degree of dissociation of the weak acid is used to characterize the acid, and is calculated according to the equation:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

where K_a is the dissociation constant. Strong acids typically dissociate completely, and therefore would have K_a greater than 1. Weak acids have K_a values much smaller than 1 (typically less than 10^{-4}). For example, the K_a of acetic acid (vinegar) is 1.75×10^{-5} , while the K_a of bicarbonate (baking soda) is 4.7×10^{-11} . For convenience, scientists often use the pK_a of weak acids, as it allows them to work with whole numbers. The pK_a 's of acetic acid and bicarbonate are 4.75 and 10.32, respectively.

When a strong base is added to a solution of a weak acid, the hydroxide ion reacts with some of the H_3O^+ present, therefore disturbing the equilibrium. More of the acid will dissociate until a new equilibrium is established. When the number of moles of base added equals the number of moles of weak acid present, a sharp change is observed in pH, which can be detected using either an indicator or pH meter. This point is the equivalence point, and any additional base added simply increases the pH. The volume and concentration of the added base can be used to determine the quantity (in moles) of acid that is present.

If the pH is measured after each small addition of base is made, a titration curve can be constructed. The titration curve allows the K_a of the acid to be determined. According to the equation above, K_a will be equal to $[H_3O^+]$ when $[A^-] = [HA]$, so the pK_a will equal the pH. This condition is met halfway to the equivalence point of the titration.

In this lab, you will determine the identity of an unknown weak acid by constructing a titration curve, estimating pK_a , and determining the equivalent molar mass of the acid based on the quantity of standard solution required.

Procedure:

Remember to record all measurements and unknown numbers in your data tables.

1. Dissolve about 1.2 grams of your acid sample in a 100 mL volumetric flask, using 0.10 M KCl solution. If it does not dissolve easily, you may *gently* heat the mixture. Allow this solution to cool to room temperature before titrating.
2. Assemble your titration setup. Rinse the buret with a few 5 mL aliquots of base before filling.
3. Set up and calibrate the pH meter. Remember to store the electrode in a pH 7 buffer solution when not in use. Also get a stir plate and place it under the buret.
4. Use a volumetric pipette to transfer 40 mL of the acid solution to a clean 150 mL beaker and place this beaker on the stir plate. Add a stir bar and place the pH electrode in the acid solution, making sure the tip is immersed. Make sure that the stir bar does not hit the electrode. Record the initial pH.
5. With stirring, add 2 mL portions of base to the acid solution, recording the pH after each addition, until the pH changes by 0.2 units. At this point decrease the volume of base added to 1 mL until the same change is observed, then 0.5 mL, then 0.1 mL as the titration proceeds through the equivalence point. Remember, the smaller the volume additions, the better equivalence point estimate.
6. Once through the equivalence point, you can increase the volumes added again. Continue the titration at least 10 mL past the equivalence point.
7. Repeat steps 5, 6 and 7.

Data Analysis:

You will need to make a plot of your titration curve data using a spreadsheet program (like Excel). The equivalence point for your titration is defined as the point of inflection (where the slope changes) on the titration curve. A rough value of V_e can be obtained by determining the point half-way up the sharp pH change. The pK_a of the acid can be determined by determining the pH value at $\frac{1}{2} V_e$, which can also be estimated from the titration curve.

The equivalence volume can be located roughly using your titration curve; a better estimate can be made using the first derivative plot of this same curve (know calculus??). The derivative is simply the slope of the line ($\Delta V/\Delta pH$) at each point on the curve). The volume of base added at the equivalence point will correspond to the maximum derivative value.

Use the following table to choose the identity of your unknown acid based on the calculated molecular weight and dissociation constant values.

Weak Acid Unknown Possibilities

Compound	Formula	Molar Mass	pKa
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	60.0	4.5
Propanoic acid	$\text{HC}_3\text{H}_5\text{O}_2$	74.1	4.9
Crotonic acid	$\text{HC}_4\text{H}_5\text{O}_2$	86.1	4.7
d/l-lactic acid	$\text{HC}_3\text{H}_5\text{O}_3$	90.1	3.9
Chloroacetic acid	$\text{HC}_2\text{ClH}_2\text{O}_2$	94.5	2.9
Potassium hydrogen oxalate	KHC_2O_4	128.5	4.2
Glutaric acid	$\text{H}_2\text{C}_5\text{H}_6\text{O}_4$	132.1	4.3
Potassium bisulfate	KHSO_4	136.2	1.9
Sodium bisulfate hydrate	$\text{NaHSO}_4 \cdot \text{H}_2\text{O}$	137.4	1.9
Adipic acid	$\text{H}_2\text{C}_6\text{H}_8\text{O}_4$	146.1	4.4
d/l-mandelic acid	$\text{HC}_8\text{H}_7\text{O}_3$	152.1	3.4
Sulfanilic acid	$\text{HC}_6\text{H}_6\text{NO}_3\text{S}$	173.2	3.2
Potassium hydrogen tartrate	$\text{KHC}_4\text{H}_4\text{O}_6$	188.1	4.3
Sodium hydrogen tartrate	$\text{NaHC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$	190.1	4.3
Sulfanilic acid hydrate	$\text{HC}_6\text{H}_6\text{NO}_3\text{S} \cdot \text{H}_2\text{O}$	191.2	3.2
Potassium hydrogen phthalate	KHC_8O_8	204.2	5.5

Name: _____ Lab Partner(s): _____

Data Sheets:

(show all work for calculations below)

Unknown #: _____

1. Mass of acid used: _____

2. Total volume of prepared acid sample: _____

3. Concentration of prepared acid sample (g/mL): _____

4. Concentration of base: _____

TRIAL 1**TRIAL 2**

5. Volume of acid titrated (mL): _____

6. Mass of acid titrated (use 3 and 5): _____

7. Equivalence Volume (V_e , from curve): _____

8. Moles of base required for equivalence: _____

9. Molar mass of unknown acid (assume 1:1 stoichiometry): _____

10. pKa of unknown acid (from curve): _____

Identity of unknown acid (use table): _____**Calculations:**

Post Lab Questions:

1.) On the titration curve you prepared, identify the equivalence point, the buffer region, and the point where $\text{pH} = \text{pK}_a$.

2.) Why is it important that you allow the heated acid solutions to cool to room temperature before titrating? What may be affected by temperature?

3.) For at least two points along your titration curve, compare the pH measured by the pH meter to the theoretical pH based on the volume of standard solution added.

4.) Explain why any differences between the values calculated in question 2 and the measured pH values may arise.

5.) Explain how you determined the identity of your unknown weak acid.